

Microgravimetric Studies of Anion Effects in the Underpotential Deposition of Copper on Platinum

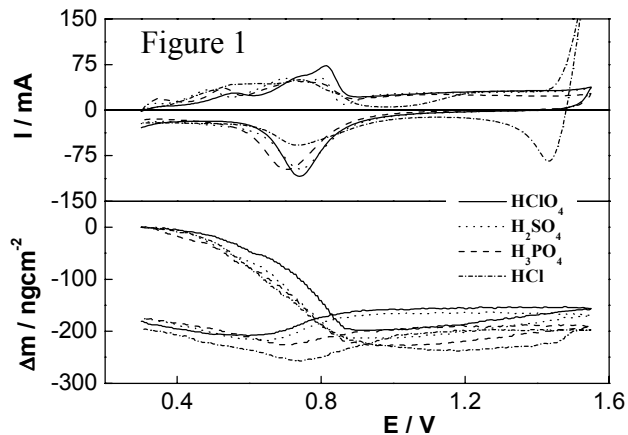
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The underpotential deposition (UPD) of metallic ions on foreign substrates is one of the more investigated subjects in electrochemistry due to its importance in several technological applications. First cycle voltammetry is the most used electrochemical technique to study UPD since it is able to detect fractions of monolayers adsorbed on the electrode. However, this technique fails in the determination of non-electroactive species such as anions co-adsorbed with ad-atoms. To overcome this limitation, the electrochemical quartz crystal microbalance (EQCM) is an interesting possibility. The simultaneous determination of charge and mass variations during the electrode process allows accounting for the species that are not active for electron transfer. In this way, the objective of this work is to study the influence of simultaneous adsorption of ClO_4^- , HSO_4^- , HPO_4^{2-} and Cl^- during the UPD of Cu on polycrystalline Pt in acid medium.

The electrolytes were 5×10^{-5} M CuO + 0.1 M of either HClO_4 , H_2SO_4 , H_3PO_4 or HCl . The Pt working electrode was assembled on an AT-cut quartz crystal with fundamental frequency of 9 MHz, geometric area of 0.2 cm^2 and roughness factor 1.75. The sensibility coefficient for the EQCM was measured as 830 $\text{Hz } \mu\text{g}^{-1}$ by Cu and Ag potentiostatic deposition. The reference electrode was the hydrogen system in the same electrolyte and the auxiliary was a 2 cm^2 Pt sheet. The experiments were performed in an EG&G PARC mod. 273A potentiostat linked with a model QCA917 Quartz Crystal Analyser, Seiko EG&G PARC.

The simultaneously recorded voltammograms and massograms for Cu UPD at 0.1 V s^{-1} in the four electrolytes are presented in Fig. 1. Here, the depositing time and potential for Cu UPD were adjusted to obtain one full monolayer in ClO_4^- (i.e., 0.3 V and 600 s). The other three electrolytes yielded amounts slightly higher than one monolayer under those conditions.



The dissolution of the Cu monolayer is observed in the potential region between 0.3 to 0.9 V. The voltammetric charges obtained from the anodic branch, in UPD region, were used to calculate the theoretical mass variation due to Cu_{ads} . These parameters are collected in Table 1, together with the experimental mass variation values.

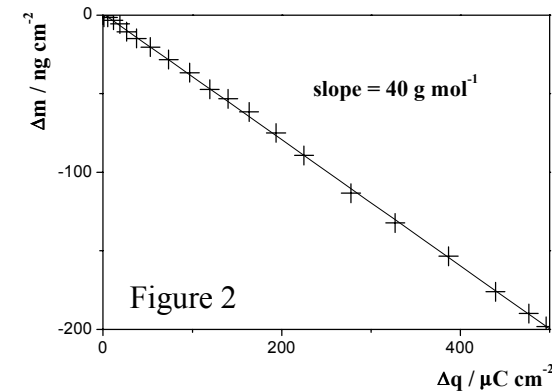
Electrolyte (0.1 M)	q_{Cu} ($\mu\text{C cm}^{-2}$)	Δm_{Cu} (calc) (ng cm^{-2})	Δm_{Cu} (exp) (ng cm^{-2})
HClO_4	425	139	198
H_2SO_4	436	143	213
H_3PO_4	490	161	226
HCl	543	178	237

The experimental values found for mass variations are significantly larger than the calculated ones. This extra mass should be attributed to adsorbed species on the UPD layer. Such species are not likely to be water, since both the metallic layer and the electrode surface are always covered with a layer of water.

To analyse the nature of this second layer, plots of Δm vs Δq were constructed using the results of Fig. 1. An example of such plot is presented in Fig. 2, for the Cu UPD in ClO_4^- .

From the charge and mass balance:

$$\Delta q_{\text{total}} = n_{\text{Cu}} Z_{\text{Cu}} F \text{ and } \Delta m_{\text{total}} = n_{\text{Cu}} M_{\text{Cu}} + (n_{\text{ClO}_4^-} M_{\text{ClO}_4^-})$$



and considering that $n_{\text{ClO}_4^-} = x^{1/2} n_{\text{Cu}}$, with x being the coverage with the adsorbed anion, each of one occupying two sites on the electrode surface:

$$\left(\frac{\Delta m_{\text{total}}}{\Delta q_{\text{total}}}\right) = \left(\frac{M_{\text{Cu}}}{Z_{\text{Cu}}}\right) \frac{1}{F} + \frac{1}{2} \left(x \frac{M_{\text{ClO}_4^-}}{Z_{\text{Cu}}}\right) \frac{1}{F}$$

the slope of Fig. 2 (40 g mol^{-1}) allows the calculation of the coverage with adsorbed ClO_4^- on the Cu monolayer surface. Here, the value found was 0.54. Application of the same procedure for the others electrolytes gives the following results: $\text{HSO}_4^- = 0.65$, $\text{HPO}_4^{2-} = 0.61$ and $\text{Cl}^- = 0.76$. These coverage values are much larger than those previously reported for the adsorption of the same anions on smooth Pt surfaces, i.e., 0.07, 0.07, 0.19 and 0.11 for ClO_4^- , HSO_4^- , HPO_4^{2-} and Cl^- , respectively [M.C. Santos, D.W. Miwa and S.A.S. Machado, *Electrochem. Comm.*, 2 (2000) 692.]. The present results indicate a stronger interaction between these anions and the Cu surface.

In this way, measurements of the charge and mass variation during Cu UPD on four different electrolytes showed the formation of a bi-layer on the Pt surface. The first epitaxial layer, adsorbed on Pt active sites, is composed only by Cu ad-atoms, as suggested by the voltammetric charge values. On the top of this layer there is another one formed by the corresponding anion. The excess mass variation observed during Cu_{ads} desorption can be associated with this by-layer formation.

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